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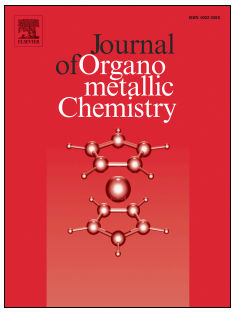

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Towards Enantiopure Macrocyclic *trans*-Dinucleating Hemilabile P-Alkene Ligands: Syntheses, Structures, and Chiral Pd-Complexes

Sibylle Frieß,[†] Alberto Herrera,[†] Anthony Linden,[‡] Frank W. Heinemann, Romano Dorta*

Department Chemie und Pharmazie, Anorganische und Allgemeine Chemie, Friedrich–Alexander–Universität Erlangen–Nürnberg, Egerlandstr. 1, 91058 Erlangen, Germany

[‡] *Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057, Zurich, Switzerland*

[†] *S.F. and A.H. contributed equally to this publication.*

Abstract

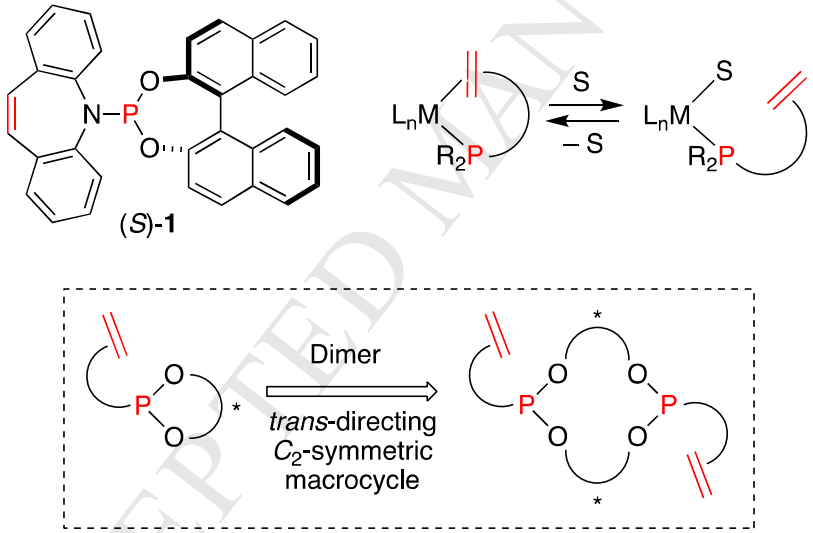
Dibenzazepinyl dichlorophosphine **2** reacts with (*R,R*)-2,3-*O*-isopropylidene-threitol (**3**) in Et_2O solution to afford gram-quantities of the enantiopure macrocylic phosphoramidite (*all-R*)-**6**, which may be seen as a formal dimer of classic phosphoramidite P-alkene hybrid ligands. Complexation experiments with $PdCl_2$ reveal highly selective formation of the *trans*-dinuclear complex (*all-R*)-**11**. The corresponding bulkier and rigidly *trans*-eclipsed 1,4-diol (*S,S*)-bis-hydroximethyl-9,10-dihydro-9,10-ethaneanthracene (**4**), does not favor macrocycle formation and exclusively leads to the new dibenzazepinyl phsophormaidite P-alkene ligand **7**, which in Pd-catalyzed asymmetric allylic amination comes the well-known 'privileged' binol-derived P-alkene analogue **1** close in terms of enantioselection.

Keywords: Chiral P-alkene ligands; Phosphoramidites; Hemilability; Chiral macrocycle; *trans*-dinuclear palladium complex; Asymmetric allylic amination

Chiral alkene ligands[1] and, in particular, chiral P-alkene ligands[2] with improved stability are well established in enantioselective catalysis. We have developed a general and facile method for the preparation of a library of dibenz[*b,f*]azepine-derived chiral P-alkene ligands.[3] One of the privileged ligand variants up to this point has been the binaphthol derivative **1** (Scheme 1),[4] which, when used in the correct ligand-to-metal stoichiometry of 2:1, displays exquisite enantioselectivities in Rh-catalyzed C–C[5] and in Ir-catalyzed[6] C–C,[7] C–N,[8] and C–O[9] bond-forming reactions. The L/M stoichiometry of 2:1 does not negatively affect catalytic performance thanks to the hemilability of

the alkene function, which has been proven in structural studies.[10] The success of ligand **1** warrants efforts directed at diversifying this architecture.[11] In the past, we have repeatedly observed the formation of byproducts during the synthesis of such phosphoramidite P-alkene ligands, which were suspected to be oligomers. Indeed, formal dimers of such molecules leading to macrocyclic tetradentate P-alkene ligands would be worthwhile synthetic targets for the formation of bimetallic complexes, which may lead to co-operative catalyst systems[12] with improved activity and selectivity.[13] However, structurally characterized chiral bimetallic complexes remain scarce, [12c, 13b] and here we wish to communicate the gram-scale syntheses of new enantiopure P-alkene ligands and, in particular, the preparation and structural characterization of a C_2-symmetric *trans*-ligated dinuclear macrocyclic palladium complex. We also show crystallographically that the alkene function of this type of ligands may or may not coordinate to Pd(II) centers.

Scheme 1. Hemilability of 'privileged' P-alkene ligand **1** and the proposed macrocyclic variant viewed as a dimer (P-alkene)$_2$

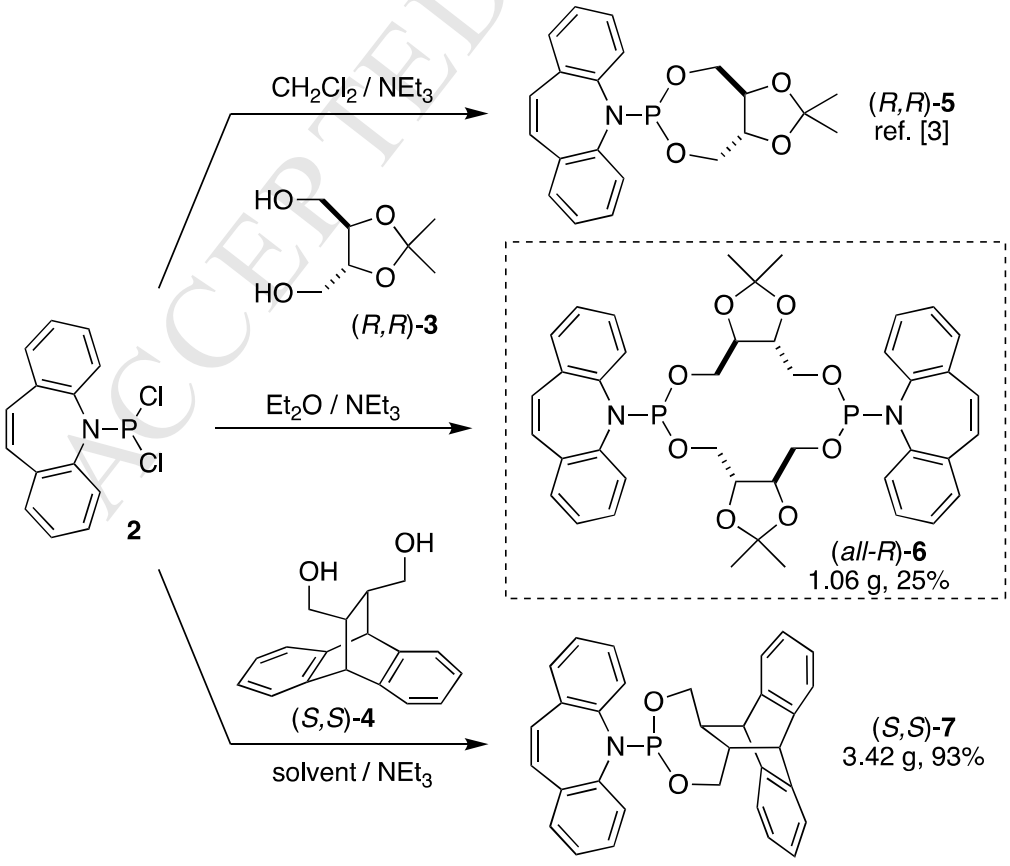


We have previously described the reaction of the dibenzazepinyl dichlorophosphine **2** with (*R,R*)-2,3-*O*-isopropylidene-threitol (**3**) in CH_2Cl_2 solution in the presence of NEt_3, which affords ligand **5** in good yields (see Scheme 2).[3] **5** shows a characteristic singlet at 139 ppm in the $^{31}P\{H\}$-NMR spectrum. However, this reaction displays a strong solvent dependency, and the use of Et_2O instead of CH_2Cl_2 typically gives a 1:1 mixture containing a new species with a ^{31}P resonance at 142 ppm.[14] This species may be separated by selective crystallization from CH_3CN solution, in which it is sparingly soluble, to afford analytically pure **6** on a gram scale. Its macrocyclic nature[15] is unambiguously established by the crystal structure of the corresponding Pd-complex **10** (*vide infra*). The ^1H-NMR spectrum of **6** shows a characteristic diastereotopic separation of the CH_3 groups resonating at 1.39 and 1.41 ppm. In view of the apparent propensity of the primary diol **3** to form

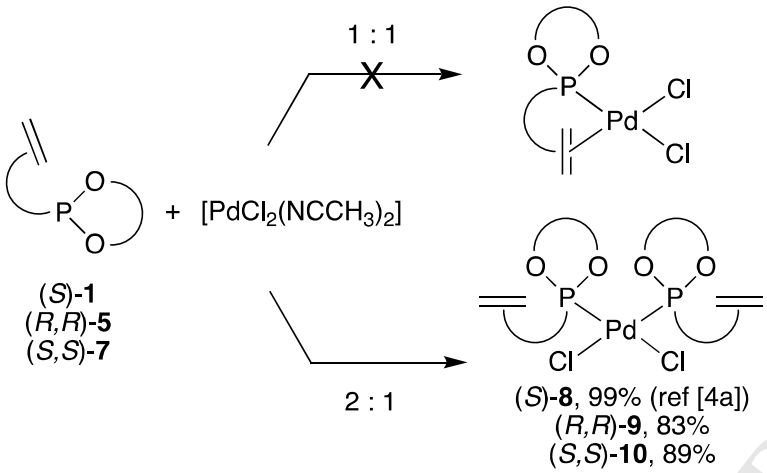
macrocycles, we were wondering if the bulky and rigidly *trans*-eclipsed primary diol (*S*,*S*)-bis-hydroximethyl-9,10-dihydro-9,10-ethaneanthracene (**4**)[16] would favor the formation of macrocyclic structures thanks to its fixed torsion angle of *ca.* 120º across the 1,4-diol backbone. Under a variety of conditions, diol **4** reacts with **2** to afford ligand **7** in high yield, but only trace amounts of the sought-after macrocyclic ligand. Therefore, it appears that diol **4** resembles binol and actually favors the formation of the rigid seven-membered dioxa-phospha cycle of P-alkene **7**.

Attempts to generate alkene-coordinated [κ^2-(P-alkene)$PdCl_2$] complexes by slowly adding any of the ligands **1**, **5** or **7** to $PdCl_2(NCCH_3)_2$ in a 1:1 stoichiometry only afforded 2:1 adducts along with 1 equiv of unreacted $PdCl_2(NCCH_3)_2$ (see Scheme 3). When reacted in the correct 2:1 stoichiometry in CH_3CN solution the respective complexes **8**–**10** form in good isolated yields. **8** has been described elsewhere,[4(a)] and **9** and **10** are free-flowing white solids, which are sparingly soluble in common organic solvents. The $^{31}P\{^1H\}$ NMR spectra of **9** and **10** show resonances at 115 and 128 ppm, respectively. Single crystals of these complexes may be grown from $CH_3CN/CHCl_3$ solution and Figure 1 shows the molecular structure of complex **10** with the expected *cis* square planar arrangement around Pd and approximate C_2 symmetry.[17] The uncoordinated C=C double bonds measure 1.352(8) Å, and the nitrogen atoms are, as expected, trigonal planar, which is typical for this ligand class when the alkene function is not coordinated to the metal center.

Scheme 2. Synthesis of enantiopure P-alkene ligands **5**–**7**



Scheme 3. Synthesis of enantiopure mononuclear Pd chloride complexes **8**–**10**



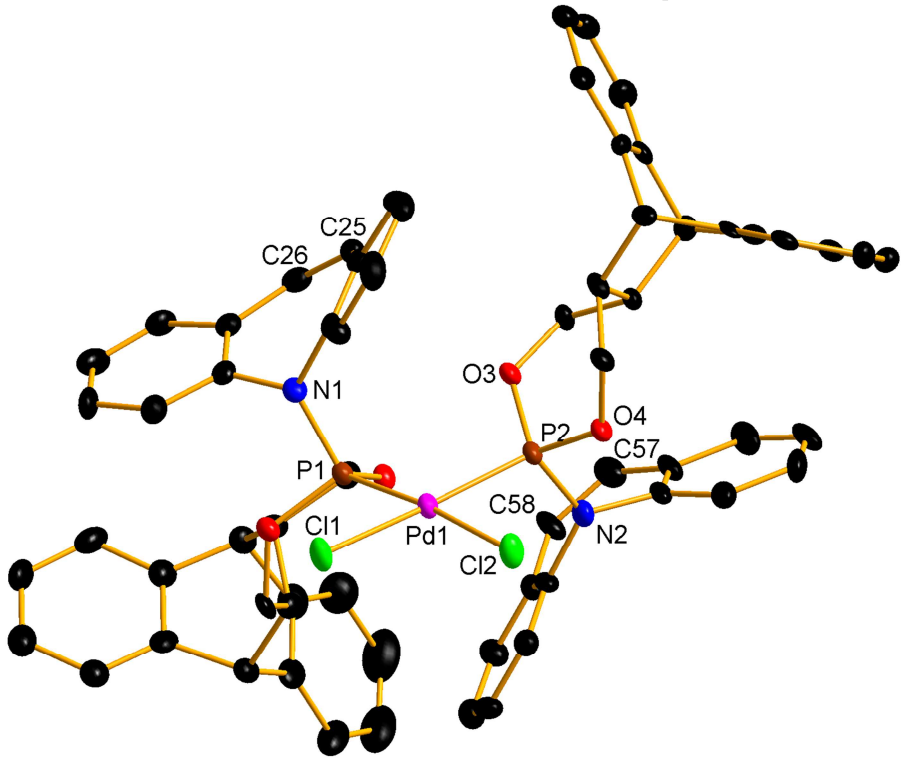
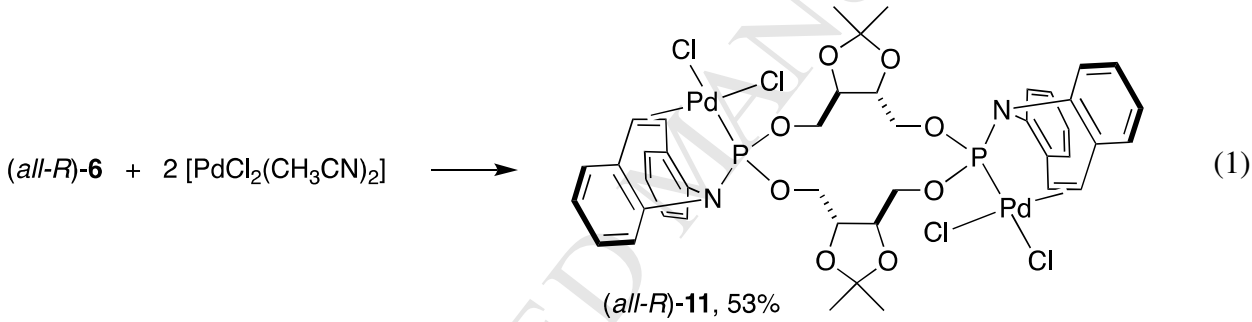


Figure 1. Molecular structure of complex **10** in the crystal (50% probability ellipsoids, H atoms are omitted). Selected bond lengths (Å) and angles (˚) are: Pd1–P1 2.226(2), Pd1–P2 2.236(2), Pd1–Cl1 2.340(2), Pd1–Cl2 2.351(2), P1–N1 1.656(6), P2–O3 1.589(5), P2–O4 1.594(5), P2–N2 1.661(6), C25—C26 1.351(11), C57—C58 1.351(12), P1–Pd1–P2 95.18(8), Cl1–Pd1–Cl2 88.49(7).

The coordination behavior of the dimeric (P-alkene)$_2$ phosphoramidite (*all-R*)-**6** is quite distinct from those of its P-alkene congeners **1**, **5**, and **7** and reacts with two equivalents of $PdCl_2(NCCH_3)_2$ according to eq 1 to form a soluble complex with a characteristic singlet at 121 ppm in the $^{31}P\{^1H\}$ NMR spectrum. A multiplet centered at 7.22 ppm in the proton spectrum hints at coordinated olefin functions, which is confirmed by the crystal structure shown in Figure 2. The chiral, C_2-

symmetrical homobimetallic complex (*all-R*)–**11** features a central 14-membered chiral diphospha-tetraoxa macrocycle that connects the two peripheral Pd atoms through its P atoms. The geometry of the ligand results in the metal centers being diametrically opposed to one another across the macrocycle. The coordination geometry of the metal centers is square planar with the chloride ligands in *cis* positions. The two chloride ligands *trans* to the alkene functions form, together with the four oxygen donors of the macrocycle, a cryptand-like structure with a pseudo-octahedral hole. Remarkably, and in contrast to structures **8**–**10**, the Pd atoms are coordinated to the alkene functions of the dibenzazepine moieties. There is no significant alteration of the coordinated C=C bonds when compared to those of the uncoordinated alkenes in complex **10**. This is in line with limited back-donation from the Pd(II) centers and the weak nature of this interaction, and compares well with similar structures.[18] Furthermore, the N-atoms adopt a pyramidal geometry (sum of angles around N1: 338.9(8)˚ and N2: 338.2(8)˚) in order to facilitate the bidentate *cis* coordination of the P-alkene function, which contrasts with the planar geometry in their monodentate coordination mode in complex **10**.



(1)

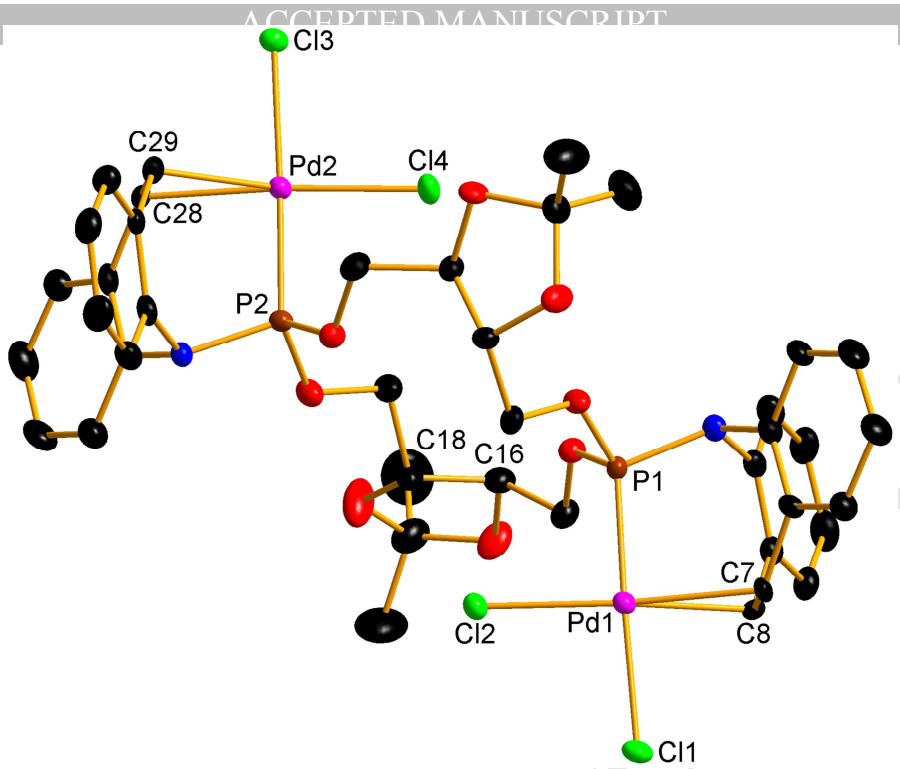
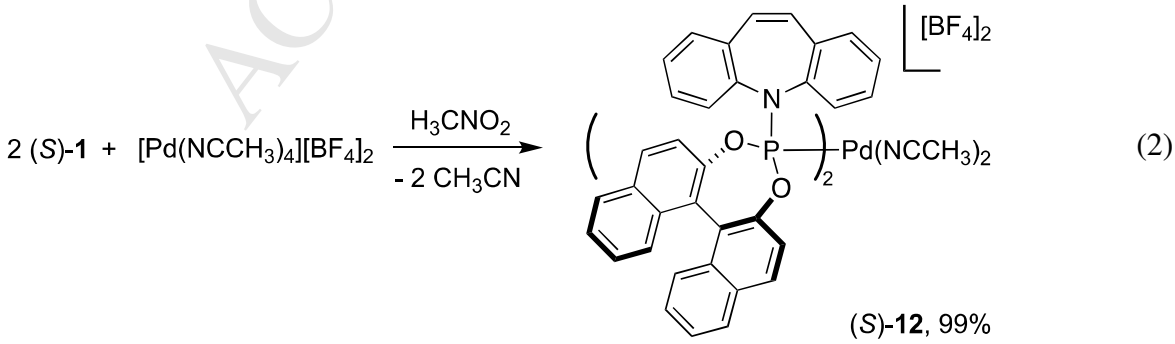


Figure 2. Structure of complex **11** in the crystal (50% probability ellipsoids, H atoms are omitted). Selected bond lengths (Å) and angles (°) are: Pd1—P1 2.1976(19), Pd1—C7 2.235(7), Pd1—C8 2.234(7), Pd1—Pd1—Cl1 2.3902(17), Cl2 2.3456(18), Pd2—P2 2.1986(19), Pd2—C28 2.222(7), Pd2—C29 2.222(6), Pd2—Cl3 2.3749(18), Pd2—Cl4 2.3380(17), C7—C8 1.381(10), C16—C18 1.516(8), C28—C29 1.385(9).

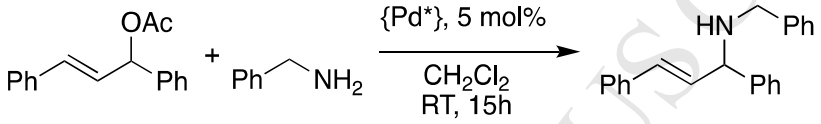
In order to provoke alkene coordination by chloride abstraction, complexes **5**–**7** were reacted with two equivalents of $AgBF_4$ in acetonitrile solution. Unfortunately, this method affords only inseparable mixtures, which could be due to competitive Ag(I)-(P-alkene) complex formation. Nevertheless, the dicationic starting complex $[Pd(NCCH_3)_4][BF_4]_2$ in combination with two equivalents of (*S*)-**1** affords analytically pure $[Pd((S)\text{-}\mathbf{1})_2(NCCH_3)_2][BF_4]_2$ ((*S*)-**12**) in almost quantitative isolated yield (eq 2). However, NMR spectra indicate no metal coordination of the alkene functions but rather the presence of two acetonitrile ligands.



(2)

Complexes **8**–**12** were benchmarked as catalysts for the asymmetric allylic amination of diphenylallyl acetate with benzylamine (see Table 1). Perhaps not surprisingly, complex **8**, which bears the privileged ligand **1**, affords the highest yield and enantioselectivity. We note that the direct use of Pd-chlorido complexes (instead of the usual *in situ* formed allylic precursors) is a viable entry into the catalytic cycle. While complex **8** gives quantitative yields, the corresponding halide-free dication **12** (entry 5) shows sluggish reactivity and no enantioselectivity. We suspect that in the latter case reduction of **12** to enter the Pd(0)-based catalytic cycle proceeds by de-coordination of the chiral ligand. Among the new ligands, **7** should be highlighted as being almost as selective as the benchmark ligand **1** (entry 3).[19]

Table 1. Complexes **8**–**12** as direct catalysts for the asymmetric allylic amination reaction



entry	{Pd*}	isolated yield (%)	e.r.
1	**8**	99	80:20
2	**9**	89	54:46
3	**10**	81	77:23
4	**11**	64	52:48
5	**12**	41	49:51

In summary, we demonstrate the feasibility of a gram-scale synthesis of the optically pure macrocyclic phosphoramidite P-alkene hybrid ligand **6** by judicial choice of the reaction solvent. We found that the increased steric bulk and rigidly *trans*-eclipsed chiral 1,4-diol backbone of **4** does not favor formation of the macrocyclic dimer against expectations but exclusively leads to the new monomeric P-alkene **7**. We are currently investigating possible template effects that favor macrocyclization of ligand **6**. From a coordination chemistry point of view, the alkene donor function in ligands **5**–**6**, which are comparable from an electronic point of view, is weak and may or may not coordinate Pd(II) centers as seen in complexes **11** and **10**, respectively. This observation indicates the typical hemilability of this ligand class. In asymmetric allylic amination, ligand **7** based on diol **4** comes close to the 'privileged' ligand **1**, which we are currently exploiting it in other catalytic applications.

Experimental Part

All reactions were carried out under anaerobic and anhydrous conditions, using standard Schlenk and glovebox techniques unless otherwise stated. Experiments without indication of temperature were performed at room temperature. THF, Et_2O, and benzene were distilled from purple Na/Ph_2CO solutions; toluene and benzylamine from Na; pentane and C_6D_6 from Na/K alloy, CH_3CN and CH_2Cl_2 from CaH_2, and NEt_3 from from K. $CDCl_3$ was degassed with three freeze-pump-thaw cycles and then kept over activated molecular sieves (4 Å) in a glovebox. NMR spectra were recorded on a JEOL 400 MHz spectrometer. (*S,S*)-**4**,[16(a)] $PdCl_2(NCCH_3)_2$,[20] $[Pd(NCCH_3)_4][BF_4]_2$,[21] complex **8**,[4(a)] and acetate **12**[22] were prepared according to a published procedure.

5,5'-((3a*R*,8a*R*,11a*R*,16a*R*)-2,2,10,10-tetramethyloctahydrobis([1,3]dioxolo)[4,5-*e*:4',5'-*l*][1,3,8,10]tetraoxa[2,9]diphosphacyclotetradecine-6,14-diyl)bis(5*H*-dibenzo[*b,f*]azepine) ((*all-R*)-6). A cool solution (*ca.* -23 °C) of (-)-2,3-*O*-isopropylidene-D-threitol (1786 mg, 11.01 mmol) in Et_2O (160 mL) was added dropwise over 20 min to a vigorously stirred, cool (-23 °C), and slightly turbid solution of **6** (3239 mg, 11.01 mmol) in Et_2O (160 mL) and NEt_3 (4.48 g, 44.3 mmol), producing large amounts of a white precipitate and a yellowish mother liquor. This mixture was stirred for 18 h, the solution filtered through a Whatman GF/B glass microfiber filter, and the white residue extracted with Et_2O (2 x 100 mL). The combined Et_2O solutions were evaporated and dried *in vacuo* leaving an off-white hard foam. CH_3CN (6 mL) was added and the yellow solution was stirred overnight to afford a white solid that was separated by filtration at -23 °C and dried *in vacuo*. Repeating this procedure with fresh CH_3CN (4 mL) yielded a white solid (1.06 g, 25 %) in 97 % isomeric purity. Elemental analysis found: C, 65.87; H, 5.65; N, 4.23; Calculated for $(C_{42}H_{44}N_2O_8P_2)(H_3CCN)_{0.25}$: C 65.69, H 5.80, N 4.06. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 3H), 1.41 (s, 3H), 3.60-3.80 (m, 6H), 6.78 (s, 2H), 7.10-7.35 (m, 8H). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 142 (s). ^{13}C NMR (101 MHz, $CDCl_3$) δ 27.2, 63.3 (d, Hz), 64.9 (d, Hz), 78.9, 109.2, 110.0, 126.3, 128.5, 129.0, 129.4, 131.2, 135.9, 142.9. The spectra show co-crystalized acetonitrile.

5-((3*R*,5a*R*)-1,5,5a,6,11,11a-hexahydro-6,11[1,2]benzenonaphtho[2,3e][1,3,2]dioxaphosphepin-3-yl)-5*H*-dibenzo[*b,f*]azepine ((*R,R*)-7): A solution of **3** (2.00 g, 7.51 mmol) in CH_2Cl_2 (130 mL) was added dropwise over 2 h to a solution of **1** (2.21 g, 7.51 mmol) and NEt_3 (3.80 g, 37.6 mmol) in 70 mL of CH_2Cl_2. After stirring for 2 h, the resulting pale yellow-green solution was evaporated under vacuum to a pale green sticky solid that was extracted with Et_2O (50 mL, then 3 x 5 mL, filtration through a G/FB filter). The solution was evacuated to dryness and after washing with cold pentane (3 x 20 mL) a white powder was obtained (3.42 g, 93%). Elemental analysis found: N 2.75, C 79.06, H 5.41; Calculated for $C_{32}H_{26}NO_2P$ C 78.84, H 5.38, N 2.87. $^{31}P\{^1H\}$ RMN (162 MHz, $CDCl_3$), δ, ppm: 140.4 s (1P). ^{1}H RMN (400 MHz, $CDCl_3$) δ 7.10 - 7.20 m (16H), 6.61 - 6.67 m (2H), 4.30 m (1H), 3.95 - 4.02 m (3H), 3.24 td (*J* = 2.93 Hz, *J* = 10.98 Hz, 1H), 3.15 m (1H), 2.32

m (1H), 2.12 m (1H). ^{13}C {^{1}H} RMN (101 MHz, $CDCl_3$) δ 145.3 (1C), 144.8 (1C), 144.4 d ($^{3}J_{C\text{-}P}$ = 5.40 Hz, 1C), 144.3 d ($^{3}J_{C\text{-}P}$ = 4.05 Hz, 1C), 139.4 (1C), 138.9 (1C), 136.3 d ($^{2}J_{C\text{-}P}$ = 13.50 Hz, 1C), 135.9 d ($^{2}J_{C\text{-}P}$ = 8.10 Hz, 1C), 131.2 (1CH), 129.2 (1CH), 129.1 (1CH), 128.8 (1CH), 128.8 (1CH), 127.9 (1CH), 127.8 (1CH), 127.7 (1CH), 127.6 (1CH), 126.17 (1CH), 126.14 (1CH), 125.9 (1CH), 125.8 (1CH), 125.7 (1CH), 125.4 (1CH), 125.0 (1CH), 122.6 (1CH), 122.5 (1CH), 71.1 ($1CH_2$), 68.3 d ($^{2}J_{C\text{-}P}$ = 8.10 Hz, $1CH_2$), 49.0 (1CH), 48.8 (1CH), 46.7 (1CH), 46.0 (1CH).

***Cis*-[$PdCl_2$((*R*,*R*)-**5**$)_2$] ((*R*,*R*)-9).** A solution of (*R*,*R*)-**5** (309 mg, 0.807 mmol) in CH_3CN (4.7 g) was added dropwise to a stirred yellow slurry of [$PdCl_2(CH_3CN)_2$] (104.6 mg, 0.4032 mmol) in CH_3CN (6.3 g) causing the precipitation of a snow white solid. The mixture was stirred for 1 h, and the solid was separated by filtration over a cotton plug and then dried *in vacuo* (315 mg, 83%, free-flowing white powder). Elemental analysis found: C, 52.44; H, 4.63; N, 2.82. Calculated for $PdCl_2C_{42}H_{44}N_2P_2O_8 \bullet H_2O$: C, 52.43; H, 4.82; N, 2.91. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ 115. ^{1}H RMN (400 MHz, DMSO-d_6, 100 ºC) δ 2.03 (s, 4H), 2.09 (s, 12 H), 3.40-3.65 (m, 8H), 6.55-6.65 (m, 4H), 6.65-6.75 (m, 12H), 6.90-7.00 (m, 4H). The spectrum indicates traces of decomposition products. No meaningful ^{13}C {^{1}H} RMN spectrum could be measured because of the low solubility of the complex.

***Cis*-[$PdCl_2$((*R*,*R*)-**7**$)_2$] ((*R*,*R*)-10).** A yellowish solution of (*R*,*R*)-**7** (500 mg, 1.03 mmol) in MeCN (7.5 mL) was added dropwise to a slurry of $Pd(MeCN)_2Cl_2$ (134 mg, 0.515 mmol) in MeCN (7.5 mL). Within a few seconds, a white precipitate formed, which was stirred for 30 min and then cooled to -33 °C for 30 min. The yellow filtrate was decanted off and the white solid was washed with cold MeCN (5 mL) and dried under HV to afford an off-white powder (526 mg, 89%). Elemental analysis found: C 66.59, H 4.47, N 2.26. Calculated $C_{64}H_{52}N_2O_4P_2Cl_2Pd$: C 66.70, H 4.55, N 2.43. ^{31}P {^{1}H} RMN (162 MHz, $CDCl_3$), δ, ppm: 89.85 s. ^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 8.31 (d, *J* = 8 Hz, 2 H), 7.44-6.91 (m, 28 H), 6.62 (d, *J* = 12 Hz, 2 H), 6.35 (d, *J* = 8 Hz, 2 H), 6.01 (d, *J* = 12 Hz, 2 H), 4.18-4.13 (m, 2 H), 3.80 (t, 4 H), 3.46 (t, 2 H), 2.94-2.82 (m, 2 H), 2.67-2.52 (m, 2 H), 1.39-1.30 (m, 2 H), 1.06-1.00 (m, 2 H) ppm. ^{13}C {^{1}H} RMN (101 MHz, $CDCl_3$) δ, ppm: 144.5, 144.0, 141.1, 139.4, 138.7, 137.9, 135.1, 131.1-125.5 (m), 123.1, 122.1, 72.2, 69.9, 45.0, 44.7, 43.3, 42.2. Colorless needles suitable for single crystal X-ray analysis were obtained by slow evaporation of a $CHCl_3$ solution.

***Cis*-[Pd_2Cl_4((*R*,*R*,*R*,*R*)-**5**)] (11).** (RD384, RD333, RD210) A solution of (*all-R*)-**5** (306 mg, 0.394 mmol) in $CHCl_3$ (3 mL) was added dropwise to a yellow slurry of [$PdCl_2(CH_3CN)_2$] (205 mg, 0.789 mmol) in $CHCl_3$ (1.5 mL) affording a clear pale yellow slightly turbid solution which was stirred for 1.5 h. The solution was filtered over a cotton plug and cooled to -33 °C for 4 days to afford lemon yellow crystals that were separated by filtration and dried *in vacuo* (232.5 mg, 53%). Elemental analysis found: C 44.82, H 3.99, N 2.42. Calculated $C_{42}H_{44}N_2O_8P_2Cl_4Pd_2$: C 44.98, H

3.95, N 2.50. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 120.4. ^1H NMR (400 MHz, $CDCl_3$) δ 1.13 (s, 3H), 1.15 (s, 3H), 3.20-3.35 (m, 1H), 3.75-3.85 (m, 1H), 3.85-3.95 (m, 2H), 4.25-4.40 (m, 1H), 4.40-4.50 (m, 1H), 7.15-7.30 (m, 2H), 7.40-7.75 (m, 8H). $^{13}C\ \{^1H\}$ RMN (101 MHz, $CDCl_3$) δ, ppm: 140.7, 134.3, 134.2, 132.7, 132.5, 130.3, 130.2, 129.6, 110.6, 110.4, 101.4, 100.7, 77.2, 75.5, 74.9, 69.9, 27.1, 26.6. X-ray quality lemon-yellow single crystals formed from a $CDCl_3$ solution (17 mg/0.6 mL) at -23 °C.

***Cis*-[Pd((*S*)-1)$_2$(NCCH$_3$)$_2$][BF$_4$]$_2$ (12).** A solution of (*S*)-**1** (684 mg, 1.34 mmol) in CH_3NO_2 (3 mL) was added dropwise to a stirred yellow solution of $[Pd(NCCH_3)_4][BF_4]_2$ (297 mg, 0.669 mmol). The resulting red solution was stirred for 2.5 h before evaporating it to dryness. The solid residue was washed and slurried with pentane (3 x 7 mL) and dried *in vacuo* to afford a red powder (918 mg, 99 %). Elemental analysis found: C, 61.28; H, 3.65; N, 3.31. Calculated $C_{72}H_{50}N_4B_2F_8O_4P_2Pd{\cdot}2H_2O$: C, 61.16; H, 3.85; N, 3.96. $^{31}P\{^1H\}$ NMR (162 MHz, NO_2CD_3) δ 92.3. ^1H NMR (400 MHz, NO_2CD_3) δ 1.3-3.5 (bm, 6H, coord NCC*H*$_3$), 5.41 (d, *J* = 7.6 Hz, 2H), 6.20-6.30 (m, 6H), 6.39 (t, *J* = 7.5 Hz, 2H), 6.80-6.90 (m, 4H), 7.00-7.10 (m, 4H), 7.15 (d, *J* = 8.4 Hz, 4H), 7.25 (t, *J* = 7.6 Hz, 2H), 7.30-7.42 (m, 4H), 7.47-7.55 (m, 3H), 7.60-7.70 (m, 4H), 8.00 (t, *J* = 8.7 Hz, 4H), 8.25 (t, *J* = 8.5 Hz, 4H). $^{13}C\ \{^1H\}$ RMN (101 MHz, NO_2CD_3) δ, ppm: 147.9, 146.1, 137.4, 135.1, 135.0, 133.3, 133.1, 132.9, 132.3, 132.1, 130.9, 130.1, 129.5, 129.3, 128.6, 128.2, 128.0, 127.7, 127.4, 127.3, 127.2, 127.1, 126.5, 121.5, 121.0, 119.7.

General procedure for the asymmetric catalytic allylic amination: *rac-trans*-1,3-Diphenylallyl acetate (0.5 mmol) and the Pd complex (0.025 mmol) were dissolved in CH_2Cl_2 (1.5 mL). After stirring for 5 min, a solution of benzylamine (1.5 mmol) in 1.5 mL of CH_2Cl_2 was added. The resulting yellow solution was stirred for 15 h at RT. The product was isolated after purification via flash column chromatography using a 19:1 mixture of hexane-EtOAc. ^1H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.4 Hz, 2H), 7.37 – 7.29 (m, 8H), 7.29 – 7.22 (m, 4H), 7.21 – 7.16 (m, 1H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.32 (dd, *J* = 15.8, 7.5 Hz, 1H), 4.39 (d, *J* = 7.4 Hz, 1H), 3.84 – 3.72 (m, 2H), 2.09 (s, 1H). Enantiomeric excess was determined by chiral HPLC (Chiralcel OD-H, hexane/isopropanol, 99:1 v/v, 0.3 mL/min, UV 260 nm), retention times: t_R = 45.07 min for the (*R*)-isomer, t_R = 47.27 min for the (*S*)-isomer.

Supplementary data

CCDC 1907446 and 1907447 contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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highlights

- A new enantiopure *trans*-dinucleating macrocylic phosphoramidite P-alkene ligand was synthesized
- Crystal structures of new chiral phosphoramidite P-alkene complexes of Pd indicate hemilability of ligand alkene functions
- The Pd complexes are single component catalysts for the asymmetric allylic amination reaction